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(54) Corrosion resistant high strength nickel-based alloy.

(57) A nickel-based alloy which has high strength and which is resistant to hydrogen embrittlement and chloride stress corrosion cracking is provided. The alloy contains 15-22% chromium, 10-28% iron, 6-9% molybdenum, 2.5 to 5% niobium, 1-2% titanium and up to 1% aluminium. Wrought products made from the alloy are useful in deep oil or gas wells for example for petroleum production tubing, and in sulphur dioxide gas scrubbers.

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Corrosion resistant high strength nickel-based alloy

The present invention relates to corrosion resistant nickel based alloys which have high strength.

Alloys having high strength, for example 689.5 MN/m^2, or advantageously even 1034 MN/m^2 are required in some applications, for sustaining stress in load bearing service in chemically adverse environments. Some plastic ductility is also needed for enduring or permitting modest amounts of deformation without sudden fracture, for example to safeguard against accidental bending, or to enable cold forming to be carried out. Alloys having this desirable combination of properties are particularly useful for use in petroleum production tubing for oil wells, in contact with chemically adverse media such as chlorides, acids and such compounds as hydrogen sulphide. The alloys must therefore exhibit resistance to corrosive pitting, stress corrosion cracking and hydrogen embrittlement, as well as high strength.

INCONEL alloy 718, as disclosed and claimed in U.S. patent 3 046 108, is an age-hardenable high strength alloy for service over a wide temperature range, from -250°C to 700°C, and offers good corrosive resistance to a wide variety of environments. Since the alloy also offers excellent stress rupture properties and fatigue strength, it has been used in down-hole service in oil wells. However the alloy has insufficient resistance to hydrogen embrittlement in the harsh environments found in "sour well" conditions, and, although having high as-cold-drawn strength, has low ductility.

The present discovery is based on the discovery of a new alloy, developed from alloy 718, which has an excellent combination of strength and ductility and which has excellent resistance to hydrogen embrittlement and chloride stress cracking.

According to the present invention there is provided an alloy consisting of, by weight 15% to 22% chromium, 10% to 28% iron, 6% to 9% molybdenum, 2.5% to 5% niobium, 1% to 2% titanium, up to 1% aluminium, the balance apart from impurities and incidental elements being nickel in a proportion of 45% to 55% of the alloy. Incidental elements which may be present in small amounts include up to 0.1% carbon, up to 0.35% silicon, up to 0.35% manganese, up to 0.01% boron, and, also, residual small amounts of cerium, calcium, lanthanum, mischmetal, magnesium, neodymium and zirconium such as can remain from additions totaling up to 0.2% of the furnace charge. Impurities present may include up to 0.5% copper, up to 0.015% sulphur and up to 0.015% phosphorus.

Commercial sources of molybdenum and niobium are often associated with tungsten and tantalum, and may be present at levels of about 0.1% tungsten and 0.1% tantalum. The tungsten level must be controlled at a low level to avoid the formation of undesired phases such as Laves phase. Although tantalum may be substituted for niobium in equi-atomic percentages, its presence is not desirable because of its high atomic weight.

The particular combination of the proportions of chromium, iron, molybdenum, niobium, titanium, aluminium and nickel give rise to desirable properties of strength, ductility, fabricability and durability in highly corrosive environments. To optimise these properties, a preferred composition contains 18.5% to 20.5% chromium, 13.5% to 18% iron, 6.5% to 7.5% molybdenum, 1.3% to 1.7% titanium, 0.05% to 0.5% aluminium, balance nickel, apart from impurities and incidental elements.

Advantageously, the titanium and niobium contents of the alloy are closely controlled such that

$\% \text{ Ti} + \frac{1}{2}(\% \text{ Nb}) \geq 3\% < 4\%$. Preferably the

alloy contains 1.3% to 1.7% titanium and 3.6% to 4.4% Nb, and most preferably 1.5% Ti and 4% Nb.

The alloy has good workability, both hot and cold, for production into wrought articles such as cold rolled strip and extruded tubing. Appropriate process treatments may be used to enhance the strengths of articles manufactured from the alloy. Such treatments include cold working, age-hardening and combinations of the two. The alloy may be annealed at a temperature of 871°C to 1149°C, and aged at 593°C to 760°C, or even 816°C. Direct aging treatments of heating the cold-worked alloy at 649°C to 760°C for from 0.5 to 5 hours directly after cold working are particularly beneficial for obtaining desirable combinations of high strength and ductility.

Alloys of the present invention, after appropriate thermomechanical processing exhibit yield strength (0.2% offset) of in excess of 1034 MN/m^2, with an elongation of 8%, and preferred alloys have strengths of more than 1310 MN/m^2 and elongation of around 15%.

Some examples will now be given.

Example 1

Three alloys of the invention and a comparative alloy were prepared. The alloy compositions are set out in Table 1.

TABLE I

CHEMICAL ANALYSES, WEIGHT PERCENTS

Alloy	Cr	Fe	Mo	Nb	Ti	Al	C	Mn	Si	B	Cu	Mg	Ni
1	20.09	17.55	7.06	3.02	1.49	0.13	0.03	0.18	0.26	0.006	NA	0.011	50.23
2	18.73	13.89	6.60	4.29	1.45	0.35	0.02	0.29	0.19	0.007	0.26	0.021	53.91
3	19.89	16.61	7.18	3.10	1.51	0.08	0.03	0.22	0.16	0.006	0.06	0.016	51.14
E	18.5	17.95	3.11	5.25	0.81	1.0	0.05	0.26	0.17	0.005	0.004	0.016	52.4

NA - Not Analysed

Cobalt, phosphorus and sulphur, when analysed, were found present in percentages of 0.011% or lower.

Niobium percentages include possible small proportions of tantalum.

Alloy 1 was prepared by vacuum induction melting and was cast to ingot form. Ingots of alloy 1 were heated at 1121°C for 16 hours for homogenization and then forged flat from 1121°C. Flats were hot rolled at 1121°C to reduce about 4 mm (0.16 gauge), annealed at 1066°C for 1 hour and cold rolled to 2.5 mm (0.1 gauge) strip, which was again annealed at 1066°C for 1 hour. Separate portions of the annealed 2.5 mm strip were cold rolled different amounts to make 1.57, 1.8 and 2.11 mm sizes (0.062, 0.071 and 0.083 gauge respectively) and then each size (including the 2.5 mm size was again annealed at 1066°C for 1 hour and cold rolled down to final gauge of about 1.27 mm (0.05 gauge) resulting in cold work reduction of about 20%, 30%, 40% and 50%.

Hardenability, including work hardenability and age hardenability, of alloy 1 was confirmed with hardness measurements, as shown in Table II, on specimens of the 1.27 mm (0.05 gauge) strip before and after heat treatments with temperatures and times referred to in the Heat Treatment Schedule (Table III).

TABLE II

Condition	Rockwell C Hardness 20% CR	30% CR	40% CR	50% CR
ACR	35	38	38.5	40
CR + HT-1	40	40	40	40.5
CR + HT-2	40.5	40.5	41.5	41.5
CR + HT-3	37	40.5	41.5	42.5
CR + HT-4	42	44	44	45
CR + HT-5	45	47	47	44.5
CR + HT-7	39.5	--	--	--
CR + HT-8	41	--	--	--
CR + HT-9	39.5	--	--	--
CR + HT-10	31.5	--	--	--
CR + HT-11	37	--	--	--

ACR - As Cold Rolled

%CR - percent reduction of thickness by cold rolling (after last anneal).

Annealed hardnesses of 20% CR strip on Rockwell B scale after treatments of 954°C for ½ hour, 1038°C for 1 hour and 1149°C for ½ hour were 97, 93 and 78.Corresponding results with 40% CR strip were 23.5 Rc, 94 Rb and 78 Rb.

TABLE III

Heat Treatment Schedule

HT-1	1038°C for 0.5 hr AC + 760°C for 8 hr FC to 649°C, hold 8 hr/AC
HT-2	954°C/0.5 hr AC + 718°C/8 - FC - 621°C/8 hr AC
HT-3	621°C/1 hr AC
HT-4	760°C/1 hr AC
HT-5	718°C/8 hr – FC - 621°C/8 hr AC
HT-6	760°C/8 hr - FC - 649°C/8 hr AC
HT-7	649°C/5 hr AC
HT-8	704°C/5 hr AC
HT-9	760°C/5 hr AC
HT-10	1149°C/0.5 hr AC + HT-5
HT-11	1149°C/0.5 hr AC + HT-6

Tensile specimens about 1.27 mm (0.05 gauge) strip of alloy 1 were evaluated for mechanical properties at room temperature in preselected thermomechanically processed conditions, including as-cold-rolled conditions and cold-rolled plus heat-treated conditions, with results set forth in the following Table IV. With cold-worked embodiments of the alloy of the invention, "direct aging", whereby the alloy is heat treated at age-hardening temperature directly (without other heat treatment intervening between cold working and aging) following cold working, gave increased yield strengths of 1034 MN/m² and higher, with good retention of ductility; moreover, the 649°C direct age provided benefits of increase in both strength and ductility exceeding 1103 MN/m² and 20% elongation.

TABLE IV

Alloy 1

Condition	Yield Strength MN/m²	Ultimate Tensile Strength MN/m²	% Elongation (2.54 cm)
ACR-20%	1022	1121	15.5
ACR-30%	1216	1283	3.5
ACR-40%	1269	1312	4.5
ACR-50%	1352	1358	3.5
20% CR + HT-7	1127	1293	21.0
20% CR + HT-8	1115	1298	15.0
20% CR + HT-9	1063	1296	14.0

The endurance of ductility of alloy 1 in a variety of conditions when subjected to hydrogen charging was tested by holding restrained 25.4 mm width cold-formed U-bend specimens at stresses greater than 100% of yield stress while being cathodically charged in a 5% sulphuric acid solution at 10 milliamps total current for 500-hour periods. Successful survival throughout the 500-hour charging periods was shown with alloy 1 in twelve processing treatment conditions,

as briefly stated below,

ACR 20%, 30%, 40% and 50%;
HT-1 following 20%, 30%, 40% and 50% CR;
20% CR plus HT-8; 20% CR plus HT-9;
20% CR plus HT-10; 20% CR plus HT-11.

In contrast, two restrained U-bend specimens of 20% cold rolled strip of alloy 1 in conditions resulting from long-time (in these instances, over 16 hours) direct age treatments HT-5 and HT-6 failed after unsatisfactorily brief survivals of 5 hours and 2 hours, respectively, when subjected to the same hydrogen charging conditions.

Good resistance to contact with acid chloride media at elevated temperatures was confirmed with evaluations of weight loss and visual appearance of specimens of alloy 1 of 10.2 cm x 7.62 cm in the 40% cold-rolled condition. Two specimens were immersed in aqueous 10% $FeCl_3$ + 0.5 HCl solutions at 66°C for 24 hours. The weight losses were satisfactorily low values of 0.03 and 0.52 mg/cm^2. Visual inspection for appearances of pitting showed that only one pit occurred and confirmed that the alloy metal provided good resistance to the acid media.

Capability of the alloy to provide resistance against stress-corrosion cracking was shown by satisfactory survival of a cold formed, restrained, U-bed specimen of 50% cold-rolled alloy 1 during a 720-hour exposure in boiling 42% $MgCl_2$.

Example 2

Alloy 2 and alloy 3 were air induction melted and centrifugally cast with protection of an argon shroud in a metal mould having a 10.8 cm I.D. and 1300 rpm rotation speed to produce cast centrifugally solidified tube shells of alloy 2 and 3. Cast dimensions were 10.8 cm O.D. and 1.9 cm wall thickness. The shell was cleaned up to 10.2 cm O.D. and 1.11 cm wall thickness.

A leader tube was welded onto the shell and processing proceeded as follows. The tube shell was annealed at 1149°C, pickled and cold drawn (about 15.8%) to 9.525 cm O.D. x 0.99 cm wall, re-annealed at 1149°C and pickled, then cold drawn to 8.89 cm O.D. x 0.889 cm wall (also 15.8% reduction), re-annealed at 1149°C and pickled, then tube reduced to 6.668 cm O.D. x 0.762 cm wall (about 36.7% reduction in area).

Mechanical properties were determined with sub-size round bar specimens taken longitudinally from the tube wall and are set out in Table V.

TABLE V

Condition	YS, MN/m²	UTS, MN/m²	% Elong (2.54 cm)	% R.A.	Hardness (Rc)
Alloy 2					
36.7% TR	1091	1157	22.0	51.0	30
36.7% TR + 704°C/1,AC	1334	1365	13.5	39.8	38
36.7% TR + 704°C/2,AC	1392	1438	14.5	42.0	40
36.7% TR + 760°C/1,AC	1368	1415	12.6	33.4	39
36.7% TR + 760°C/2,AC	1390	1422	12.5	33.9	40
36.7% TR + 1038°C/1, AC + HT - 5	1044	1351	31.6	50.5	34
Alloy 3					
36.7% TR	1042	1119	17.5	53.8	30
36.7% TR + 704°C/1,AC	1234	1322	16.5	44.2	36
36.7% TR + 704°C/2,AC	1255	1342	15.0	48.5	37
36.7% TR + 760°C/1,AC	1244	1313	13.6	39.9	37.5
36.7% TR + 760°C/2,AC	1278	1348	13.5	31.4	37.5
36.7% TR + 1038°C/1, AC + HT - 5	924	1286	28.6	49.2	32.0

R.A. - Reduction in Area

Good combinations of strength and ductility are achieved with cold-worked and direct-aged articles of alloys 2 and 3, especially with one to two hour direct ages at 704°C to 760°C.

A transverse specimen taken from the extruded

and 704°C direct aged product of alloy 3 was of ASTM grain size No. 3½ ; optical microscopy of the specimen showed an absence of intergranular carbides and indicated that the extruded, cold-reduced and heat-treated microstructure did not contain any intra-granular phases resolvable at 1000x.

Example 3

Alloys 2, 3 and E were melted, and centrifugally cast to tube shells and processed to 6.67 cm O.D. tube with 0.762 cm wall thickness by the process described in Example 2. Table VI compares chloride stress corrosion cracking data for these alloys at 177°C and 204°C. The alloy samples were prepared as stressed C-ring specimens and subjected to a simulated deep sour gas well environment comprising a 25% solution of sodium chloride plus 0.5% acetic acid and 1 g/l sulphur, the solution saturated with hydrogen sulphide to an H_2S overpressure of 861 KN/m^2.

TABLE VI

Alloy	Temperature °C	MN/m^2 Test stress	life (days)	Material condition
E	177	1220 (1)	45-57	37% cw
3	177	1275	*>68	37% cw + 760°C/2 hr, AC
E	204	986	<22	37% cw + Anneal + Age (2)
2	204	1089	>42	37% cw
2	204	1248	>65	37% cw + 649°C/1 hr,AC
3	204	1275	>42	37% cw + 760°C/2 hr,AC

(1) This test was run at 90% of 0.2% offset yield strength at RT. All others were run at 100%.

(2) 1038°C/1 hr AC + 718°C/8 hr FC at 55.6°C/ hr to 621°C/8 hr AC.

* > denotes test discontinued at number of days shown with no failure.

The test conditions chosen for alloy E were those considered to be less prone to hydrogen embrittlement

than the cold worked + aged samples of alloys 2 and 3. Despite testing at lower stress the comparative alloy failed earlier than alloys of the invention.

Hydrogen embrittlement tests were carried out on stressed c-ring specimens of the alloy coupled to steel in solution of 5% sodium chloride + 0.5% acetic acid, saturated with hydrogen sulphide. Results are shown in Table VII.

TABLE VII

Alloy	Test stress MN/m^2	% of R.T. Yield Strength	Life (days)	Condition
E	1289	95	<3	37% CW
E	1206	90	<6	37% CW
3	1275	100	>42	37% CW + 760°C/ 2 hrs, AC
3	1206	100	>42	37% CW + 788°C/ 1 hr, AC.

The room temperature tensile data corresponding to the above corrosion data is summarised in Table VIII.

TABLE VIII

Room Temperature tensile results

Alloy No.	Condition	Hardness Rc	0.2 Yield strength MN/m^2	Tensile strength MN/m^2	Elong. %	R.A. %
E	37% CW	37.5	1358	1413	8	31
E	37% CW + anneal + age (1)	34	986	1289	24	41
2	37% CW	30	1089	1158	22	51
2	37% CW + 649°C/ 1 hr, AC	-	1248	1351	19	50
3	37% CW + 760°C/ 2 hr, AC	37	1344	1344	13	31
3	37% CW + 788°C/ 1 hr, AC	36	1206	1296	16	35

(1) 1038°C/1 hr, AC + 718°C/8 hr FC at 55.6°C/hr to 621°C/8 hr, AC.

It will be observed that the commercial alloy E has very high as cold drawn strength and low ductility,

and this was why alloy E was tested in corrosion tests at a stress less than 100% of RT yield strength.

It will be noted from the comparison between alloys 2, 3 of the present invention and the commercial alloy E that the special correlation of composition of the present invention gives rise to enhanced corrosion resistance in respect of chloride stress corrosion cracking and hydrogen embrittlement. At the same time however the alloys of the invention exhibit a desirable combination of strength and ductility.

Alloys of the present invention are useful for tubes, vessels, casings and supports, needed for sustaining heavy loads and shocks in rough service while exposed to corrosive media, and particularly for production tubing to tap deep natural reservoirs of hydrocarbon fuels. In deep oil or gas well service, possibly in off-shore installations, the alloys are beneficial for resistance to media such as hydrogen sulphide, carbon dioxide, organic acids and concentrated brine solutions sometimes present with petroleum. Also, the alloys provide good resistance to corrosion in sulphur dioxide gas scrubbers and are useful for seals, ducting, fans, and stack lines in such environments. Articles of the alloy can provide useful strength at elevated temperatures up to 648°C and possibly higher.

Claims

1. A high strength corrosion resistant alloy consisting of, by weight, 15 to 22% chromium, 10 to 28% iron, 6 to 9% molybdenum, 2.5 to 5% niobium, 1 to 2% titanium, up to 1% aluminium, the balance apart from impurities and incidental elements being nickel in a proportion of 45 to 55% of the alloy.

2. An alloy as claimed in claim 1 wherein the amounts of titanium and niobium are correlated in accordance with the relationship $\%Ti + \frac{1}{2}(\%Nb) > 3 < 4$.

3. An alloy as claimed in claim 2 containing 1.3 to 1.7% titanium and 3.6 to 4.4% niobium.

4. An alloy as claimed in any preceding claim consisting of 18.5 to 20.5% chromium, 13.5 to 18% iron, 6.5 to 7.5% molybdenum, 1.3 to 1.7% titanium, 0.05 to 0.5% aluminium, balance nickel apart from incidental elements and impurities.

5. A wrought product comprising an alloy as claimed in any preceding claim which has been hot worked or cold worked, and heat treated to develop a yield strength (0.2% offset) of in excess of 1034 MN/m^2 and an elongation of greater than 8%.

6. A wrought product as claimed in claim 5 which is annealed at a temperature in the range 871° to 1149°C and aged at a temperature in the range 593° to 816°C.

7. A wrought product as claimed in claim 5 which has been produced by cold working and has been aged at a temperature in the range 649°C to 760°C for from 0.5 to 5 hours after cold working.

8. A wrought product as claimed in any one of claims 5 to 7 which after thermomechanical processing exhibits a yield strength of greater than 1310 MN/m^2 and an elongation of 15% or more.

9. Use of a wrought product as claimed in any of claims 5 to 8 for parts in deep oil or gas well service, or in sulphur dioxide containing environments.